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Published in:
Physical Review B

DOI:
10.1103/PhysRevB.57.4764

Publication date:
1998

PHYSICAL REVIEW B VOLUME 57, NUMBER 8 15 FEBRUARY 1998-II

Roughness effects on the sliding frictional force of submonolayer liquid films on solid substrates

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(Received 18 August 1997)

The sliding frictional force of a liquid submonolayer in contact with a random rough surface in an oscillatory motion is considered. The frictional force is proportional to the square of the sliding velocity v, $F_f \sim v^2$, with a proportionality factor that depends on the particular roughness configuration. Analytic calculations are performed for self-affine roughness characterized by the roughness exponent $0<H<1$, the roughness amplitude Δ, and the correlation length ξ. The proportionality factor is shown to decrease with increasing H and decreasing ratio Δ/ξ, following a power law $\sim\Delta/\xi^H$. [S0163-1829(98)01608-7]

I. INTRODUCTION

The problem of friction, adhesion, and lubrication at solid-liquid interfaces has attracted enormous attention because of its fundamental and technological importance.[1] The surface force apparatus[2] and atomic force microscope[3]) have facilitated enormous advances in understanding the phenomenon of friction, since they allow one to study contacts at microscopic length scales. In addition, the quartz crystal microbalance (QCM) has been used successfully to study frictional forces between a surface and an adsorbed film at various monolayer coverages.[4] Efforts to describe the microscopic features of friction have been pursued in terms of various theoretical approaches.[5] Nevertheless, despite the insight into the phenomenon of friction provided by molecular dynamics simulations and analytic models, fundamental understanding still remains incomplete.

A characteristic common theme of many theoretical treatments is the consideration of atomically flat surfaces. However, real surfaces always have some degree of surface roughness which depends on the specific material and the method of surface treatment. Experimentally, it has been shown that surface roughness may have a strong effect on the frictional forces in confined geometry systems.[6] For a thin liquid film (significantly thicker than a monolayer) confined between two rough walls where a three-dimensional liquid flow is generated by moving one of the walls, the frictional forces can be strongly influenced by the presence of wall roughness, which can lead to frictional forces with memory (nonlocal in time).[7] This study focused on the case where the first one or two liquid layers next to the underlying substrate became locked to the solid wall, effectively ignoring slippage effects on the moving wall.

Furthermore, the influence of surface roughness between a thin liquid layer on top of a rough surface that oscillates back and forth (i.e., QCM studies) still remains in its infancy, since a continuous theory that takes the roughness effect properly into account has not yet been developed. In our study, we will show in terms of a semiphenomenological treatment that the sliding frictional force F is proportional to the square of the velocity ($\sim v^2$). In vector notation $\mathbf{F}=-k|\mathbf{v}|\mathbf{v}$ where $\mathbf{v}$ is the velocity of the film relative to the substrate. The proportionality constant k depends on the particular roughness morphology. Finally, analytic calculations of the roughness effect on the frictional force will be performed for random self-affine roughness which is observed in a wide variety of nonequilibrium growth studies of thin solid films[8] that can be potential substrates to probe frictional laws at a molecular level on rough surfaces.[4]

II. SLIDING FRICTIONAL FORCE OF SUBMONOLAYER FILMS

In general, as a starting point to examine the phenomenon of friction, the following alternate forms of frictional laws can be invoked. *Amonton's law* $F=-\mu N$, with μ and N respectively the kinetic coefficient of friction and the normal force,[9] *Stoke's law* $F=-bv$, with b a constant coefficient of friction;[10] and finally *Newton's law* $F=-cv^2$, with c a constant coefficient of friction.[10] In the latter case, the existence of such a law over a curved surface, under the assumption that the frictional force is proportional to the normal force, is anticipated. This is because the normal force is effectively the ''centrifugal force'' ($\sim v^2$).

Although it is typical to use Amonton's law for the case of a block sliding on a plane, its application to a monolayer or submonolayer film is not immediately obvious. For a block sliding on a plane, it is widely believed[11] that the normal force increases the contact area between the block and the plane. The increased contact area yields the frictional force law $F=-\mu N$. Amonton's law must be viewed differently for submonolayer films sliding on a substrate.

Our physical picture may be described as follows: Consider first (for simplicity) a single atom sliding along a substrate. If a normal force is applied, pushing the atom down into the substrate, then the substrate corrugation potential is increased. The atom now transfers more of its energy into the vibrational energy of the substrate. Thus a normal push downward increases the corrugation potential strength along with the vibrational heating of the substrate. This represents an increased friction force. If the normal force on the atom is upward, pulling the atom away from the substrate, then the atoms on the substrate are also pulled upwards toward the sliding atom. The upwardly pulled substrate atoms ''feel'' a van der Waals attraction to the sliding atom. The nonequilibrium displacement of these attracted substrate atoms again increases the vibrational substrate heating. Thus we expect increased vibrational heating for submonolayer films whether the films are pushed toward or pulled away from the ''natural equilibrium distance'' from the substrate surface. The natural equilibrium distance corresponds to zero normal force. Note that, in the case of Amonton's law for a block sliding on a plane, only a normal force pushing the block into the plane increases the friction force.

Therefore, one may conjecture that the sliding friction for a monolayer would increase as the normal force becomes stronger (substrate-adsorbate van der Waals interactions).[4] Thus, as will be shown in the following, if this conjecture is correct then Newton's law follows from Amonton's law if the substrate surface is rough.

The fluid mechanics of a submonolayer film sliding over a rough surface requires for its formulation the notions of differential geometry introduced by Gauss.[12,13] In fact, the position vector R of a point on the surface is determined by the local coordinates (x^1,x^2). The tangent vectors on the surface are defined by $e_m=\partial_m R$ with $g_{mn}=e_m e_n$, and the unit vector normal to the surface by $\hat{n}=(e_1 x e_2)/\sqrt{g}$ $(g=g_{11}g_{22}-g_{21}g_{12})$. Moreover, the connection coefficients Γ^i_{mn} and the Gaussian curvature matrix elements b_{mn} are defined, respectively, by $d\hat{n}\ dR=-b_{mn}dx^m dx^n$ and $\partial_m\partial_n R=\Gamma^i_{mn}e_i+\hat{n}b_{mn}$.

The fluid velocity of the film is given by $v=v^m e_m$ where the Einstein convention is used for repeated indices, and their spatial derivatives are given by $\nabla_i v^m=\partial_i v^m+\Gamma^m_{in}v^n$ in order to transform as tensors. The form of fluid mechanics changes when viewing the temporal variations of the fluid momentum, since there exists a force on the film normal to the substrate which is related essentially to the surface curvature. The force per unit area on the film obeys the equation

$$F=\rho[(\partial v^m/\partial t+v^n\nabla_n)v^m\Gamma^m_{ni}v^n v^i]e_m+\rho(b_{mn}v^m v^n)\hat{n}, \tag{1}$$

with ρ the two-dimensional mass per unit area. Since the principal radii of curvature $(r_{1,2})$ are determined by the eigenvalue problem $\det\|b_{mn}-(1/r)g_{mn}\|=0(g_{mn}=e_m e_n)$, we obtain $b_{mn}v^m v^n=(v^2/r_{ef})$. The latter implies that the last term on the right-hand side of Eq. (1) is the normal force per unit area arising from a ''local circular motion'' acceleration. Therefore, by applying Amonton's law (frictional force proportional to the normal force), we obtain, from the normal force component $[\sim\rho(b_{mn}v^m v^n)\hat{n}]$ in Eq. (1), the frictional force per unit area

$$F_f=\mu_f\rho|b_{mn}v^m v^n|, \tag{2}$$

which stems from the curvature argument with μ_f, the friction coefficient. The nature of the liquid-surface interaction is effectively responsible for the film formation on the underlying substrate, and is reflected by the two-dimensional mass per unit area ρ in Eq. (2). If the substrate underlying the adsorbed film oscillates back and forth (e.g., as in QCM studies), then film slippage effects can be probed by the inertial reaction forces which the film presents to the oscillator.[4]

In what follows, the coordinates of the rough surface will be taken as $(x^1,x^2)=(x,y)$, with x and y the plane coordinates seen by an observer looking straight down to the rough surface with height profile $z=z(x,y)$. For a surface with random roughness, Eq. (2) should be ensemble averaged over possible roughness realizations: $F_f\sim\langle|b_{mn}v^m v^n|\rangle$. Moreover, we assume the height profile function $z(x,y)$ to follow a Gaussian distribution.[14] Taking into account the identity $\langle|W|\rangle=[(2/\pi)\langle|W|^2\rangle]^{1/2}$ which is valid for a Gaussian random variable W, Eq. (2) in the weak roughness limit $(|\nabla z|\ll 1)$ finally yields

$$F_f\cong\mu_f\rho\left[\frac{2}{\pi}\left\langle\left(\frac{\partial^2 z}{\partial x^2}\right)^2\right\rangle\right]^{1/2}v^2, \tag{3}$$

assuming the underlying surface to move in the x direction (which effectively will also constrain the film to move on the average in the same direction). In Eq. (3) the parameter v is the film velocity relative to the substrate, which becomes an average over the microscopic motion of the film particles,[4] and in general is not constant.

Furthermore, if we define the Fourier transform of $z(r)$ by $z(r)=\int z(q)e^{-i\mathbf{q}\cdot\mathbf{r}}d^2q$, we obtain

$$\left\langle\left(\frac{\partial^2 z}{\partial x^2}\right)^2\right\rangle=\int q_x^2 q_{x'}'^2\langle z(q)z(q')\rangle e^{-i(q+q')-r}d^2q\ d^2q', \tag{4}$$

which can be simplified further by considering translation invariant surfaces or $\langle z(q)z(q')\rangle=[(2\pi)^4/A]\langle|z(q)|^2\rangle\delta^2(q+q')$. Upon substitution into Eq. (4), we finally obtain

$$F_f\cong\mu_f\rho\left[(32\pi^3/A)\int_{0<q<q_c}q_x^4\langle|z(q)|^2\rangle d^2q\right]^{1/2}v^2, \tag{5}$$

with A the average macroscopic flat surface area. In Eq. (5) only the knowledge of the roughness spectrum $\langle|z(q)|^2\rangle$ is required to calculate further the roughness contribution.

III. RESULTS FOR SELF-AFFINE ROUGHNESS

The roughness spectrum $\langle|z(q)|^2\rangle$ for any physical self-affine fractal surface is characterized by a finite correlation length ξ (which is a measure of the average distance between consecutive peaks and valleys on the surface) such that[15,16]

$$\langle|z(q)|^2\rangle\propto\begin{cases}q^{-2-2H} & \text{if } q\xi\gg 1\\ \text{const} & \text{if } q\xi\ll 1.\end{cases} \tag{6}$$

The roughness exponent H $(0<H<1)$ is a measure of the degree of interface irregularity at small length scales $(<\xi)$ (Refs. 13–15), such that as H becomes smaller the surface becomes more jagged, and is associated with a local fractal dimension $D=3-H$.[17] The scaling behavior of $\langle|z(q)|^2\rangle$ [Eq. (6)] is satisfied by the simple analytic model[18]

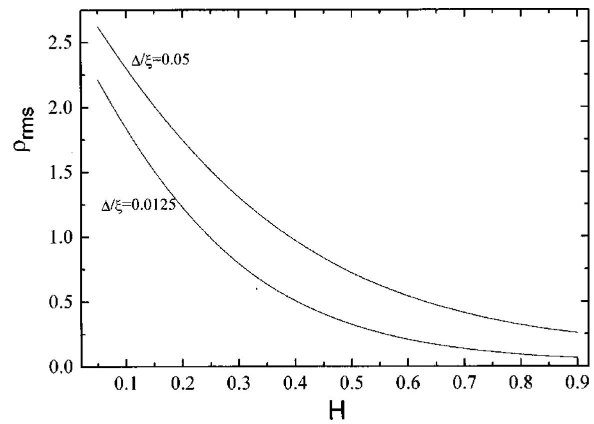

FIG. 1. Schematics of the local surface slope $\rho_{\mathrm{rms}}=\langle|\nabla z|^2\rangle^{1/2}$ vs H for $a_0=0.3$ nm, $\Delta=1.0$ nm, and ξ=20 and 80 nm.

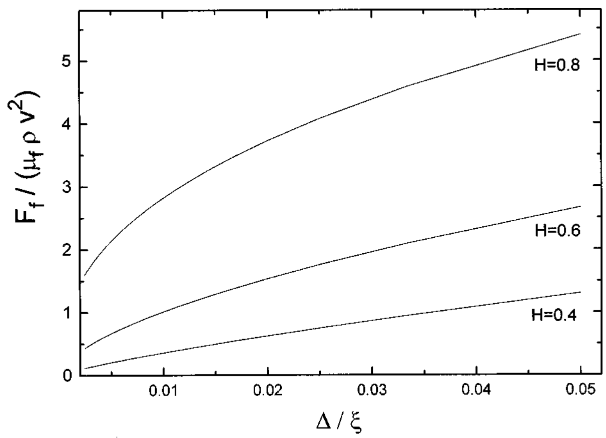

FIG. 2. Schematics of the sliding frictional force $F_f/\mu_f\rho v^2$ vs Δ/ξ for $a_0=0.3$ nm, $\Delta=1.0$ nm, and $H=0.4$, 0.6, and 0.8.

$$\langle|z(q)|^2\rangle=\frac{A}{(2\pi)^5}\frac{\Delta^2\xi^2}{(1+aq^2\xi^2)^{1+H}}, \tag{7}$$

where $\Delta=\langle z(x,y)^2\rangle^{1/2}$ is the rms roughness amplitude. The parameter a is given by $a=(1/2H)[1-(1+aq_c^2\xi^2)^{-H}]$ if $0<H\leqslant 1$, and $a=1/2\ln(1+aq_c^2\xi^2)$ if $H=0$ (logarithmic roughness). $q_c=\pi/a_0$, with a_0 a low cutoff to the order of the interatomic spacing where any continuum notion cease to exist.[18,19]

Upon substitution of Eq. (7) into Eq. (5), we obtain the analytic expression for the frictional force,

$$F_f\cong\mu_f\rho[(3\pi)^{1/2}/4a^{3/2}](\Delta/\xi^2)[\Phi(H,\xi)]^{1/2}v^2, \tag{8}$$

$$\Phi(H,\xi)=(2-H)^{-1}(X_c^{2-H}-1)+[2(H-1)^{-1}](X_c^{1-H}-1)$$
$$+H^{-1}(1-X_c^{-H}), \tag{9}$$

with $X_c=1+aq_c^2\xi^2$. In the limit of non-self-affine cases for $H=0$ and 1, we obtain $\Phi(0,\xi)=\frac{1}{2}(X_c^2-1)-2(X_c-1)+\ln(X_c)$ for $H=0$, and $\Phi(1,\xi)=\frac{1}{2}(X_c-1)+2\ln(X_c)+(1-X_c^{-1})$ for $H=1$, respectively.

Our calculations of the roughness effect on the sliding frictional force were considered in the weak roughness limit ($|\nabla z|\ll 1$). An effective condition of the latter could be that the rms local surface slope $\rho_{\mathrm{rms}}=\langle|\nabla z|^2\rangle^{1/2}$ is sufficiently small ($\ll 1$). As was shown in earlier studies,[20] the rms local surface slope is given in terms of Eq. (5) by the analytic relation $\rho_{\mathrm{rms}}=(\Delta/\sqrt{2}a\xi)[(1-H)^{-1}(X_c^{1-H}-1)+H^{-1}(X_c^{-H}-1)]^{1/2}$. Schematics of ρ_{rms} vs H for various long-wavelength roughness ratios Δ/ξ are shown in Fig. 1. Thus, our calculations of the frictional force will be performed for roughness parameters $(H,\Delta/\xi)$ such that $\rho_{\mathrm{rms}}=\langle|\nabla z|^2\rangle^{1/2}\ll 1$.

Indeed, we expect qualitatively that as the roughness exponent becomes large ($H\sim 1$) and/or Δ/ξ becomes small ($\ll 1$), the frictional force due to surface curvature will decrease, since the underlying surface will be smoother. In Fig. 2, where we present $F_f/\mu_f\rho v^2$ vs Δ/ξ for three distinct roughness exponents H, the intuitively expected behavior is attained. Alternatively, the effect of the roughness exponent H on $F_f/\mu_f\rho v^2$ is shown in Fig. 3. From both schematics we can infer that, between the roughness parameters Δ, ξ, and H, the sliding frictional force is more sensitive to the roughness exponent H, which describes fine roughness details (degree of surface irregularity or jaggness) at short wavelengths ($<\xi$).

For $\xi\gg a_0$ and $0<H<1$, we obtain $\Phi(H,\xi)\approx(2-H)^{-1}a^{2-H}(q_c\xi)^{4-2H}$ since $q_c\xi\gg 1$, and finally the frictional force

$$F_f\approx\mu_f\rho T(H)(\Delta/\xi^H)v^2, \tag{10}$$

with $T(H)=[(3\pi)^{1/2}(a^{1/2}q_c)^{2-H}]/[4a^{3/2}(2-H)^{1/2}]$. Thus the roughness contribution on the sliding frictional force scales in the self-affine regime (to leading order) as $\sim\Delta/\xi^H$ which explains its sensitivity to the roughness exponent H. Note also that similar scaling behavior is observed on the rms local surface slope $\rho_{\mathrm{rms}}\sim\Delta/\xi^H$.[20]

IV. CONCLUSIONS

In conclusion, we showed that if the frictional force is proportional to the normal force, from Amonton's law we obtain Newton's law for the frictional force of a submonolayer liquid film sliding on a random rough surface (F_f

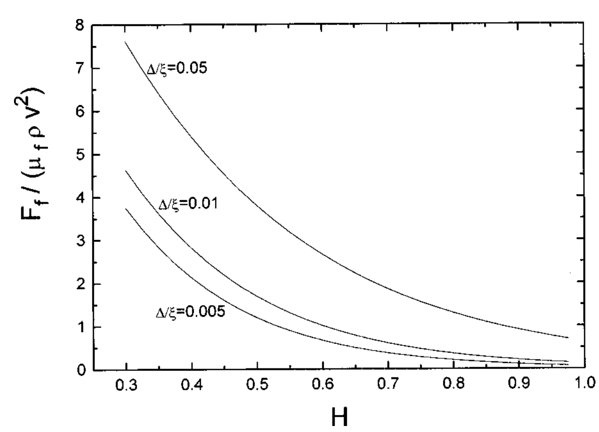

FIG. 3. Schematics of the sliding frictional force $F_f/\mu_f\rho v^2$ vs H for $a_0=0.3$ nm, $\Delta=1.0$ nm, and ξ=40, 100, and 200 nm.

$\sim v^2$). Our calculations were performed for self-affine random roughness in the weak roughness limit assuming a Gaussian surface height distribution. It was found that among all the roughness parameters, the frictional force is more sensitive to the roughness exponent H which characterizes the degree of surface irregularity at short length scales ($<\xi$).

ACKNOWLEDGMENTS

We would like to acknowledge helpful discussions with J. Krim and J. B. Sokoloff. G.P. acknowledges support from the Department of Applied Physics at Delft University of Technology.

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